Time-Resolved Luminescence of DNA-Bound Imide and Diimide Electron Acceptors *	U9B

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Imide and diimide chromophores have been designed and synthesized with functional groups to optimize their non-covalent association with DNA. Specifically, naphthalene and benzophenone derived imides and diimides have been shown to associate strongly with calf thymus DNA and nucleic acid homopolymers. From DNA-induced spectral changes in the ultraviolet and visible spectral regions, binding constants have been obtained. The association constants vary in the range of 1 x 10^4 to 5 x 10^6 M^{-1}, depending upon the chromophore and nucleic acid polymer employed. Nanosecond laser flash photolysis methods are being employed to characterize the reactive intermediates produced upon excitation of the DNA-bound chromophore. From these investigations, the imide or diimide radical anion is clearly produced, suggesting that oxidative damage to the DNA is occurring. In conjunction with these studies, luminescence spectroscopy at U9B is being employed to deduce the photophysical properties of DNA-bound chromophores. Specifically, the simultaneous timing and spectral detection capabilities of the "Fluorescence Omnilyzer" are employed to obtain and resolve the fluorescence and phosphorescence spectra and lifetimes of the chromophores in aqueous solution and bound to DNA. The results of the luminescence studies suggest that, in aqueous solutions of the chromophore and base monophosphate, the electronically excited triplet state is quenched to produce the oxidized base and imide radical anion. Conversely, when the chromophores are bound to DNA, the electronically excited singlet state is responsible for the base oxidation. The results of these studies are being used to design more effective chromophores that are capable of initiating oxidative damage to DNA. To date, we have characterized three imide-derived chromophores and demonstrated that, depending upon the thermodynamic properties of the dye, chemical specificity can be obtained to selectively oxidize specific base sites.

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